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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON

Letter
Circular
LC630

February 1, 1941

BLUING OF IRON AND STEEL

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BLUING OF IRON AND STEEL

I. INTRODUCTION

The bluing of iron or steel is the subject of frequent inquiries, for replies to which this letter circular has been prepared. Many formulas and methods have been described in the technical literature. The results of a survey of these methods form the basis of this letter circular. Only the favorably reported methods for the direct bluing have been included, and no tests were made with indirect methods, such as those requiring the electroplating of the steel with another metal and the subsequent bluing of that metallic surface. Similarly this report does not include any study of coloring by painting, enameling, or other coating methods.

The conclusions reached and the recommendations expressed are based on tests made on the following materials:- open-hearth iron, SAE 1020 steel, SAE 1045 steel, SAE 10105 steel, SAE 2335 steel and gray cast iron. Specimens about 1/2 inch in diameter and 1/4 inch thick were used, with one face polished by successively finer emery papers, and finished with levigated alumina on a broadcloth covered wheel, such as is used in metallographic work.

Care should be taken in handling the chemicals used in metal coloring, as some of them and their reaction products are poisonous. Adequate ventilation should be provided so that the worker does not inhale the vapors or gases evolved during the coloring.

II. INFLUENCE OF SURFACE CONDITIONS ON THE COLORING.

1. Surface finish.

The uniformity and general appearance of the color depends considerably on the character of surface finish of the steel previous to the bluing operations. Bright shining colors are produced only on well-polished surfaces. An abraded or mat surface always appears a little darker than a polished surface colored by the same method. Slight variations, however, are less noticeable on an abraded or mat surface. The brightness or luster can, therefore, be controlled to a great extent by a suitable choice of the finishing operation preceding the coloring.

2. Cleanliness of the surface.

Uniformity of coloring is greatly influenced by the initial cleanliness of the surface. Grease, rust, or any adherent foreign particles usually shield portions of the surface against the chemical action and lead to uneven coloring. Sometimes a very unsatisfactory spotted appearance is produced. Care must be taken to avoid any contact of the hands with the surface during the cleaning or bluing operations. The articles should be supported by wires, or handled in wire baskets or with suitable tongs. Any surface rust should be removed early in the cleaning operations.

The three methods 8 * in general use for cleaning metals contaminated with grease or polishing compounds employ organic solvents, such as trichloroethylene, ethylene chloride, orthodichlorobenzene or carbon tetrachloride; emulsifiable solvent cleaners, such as sulphonated corn or castor oil, or triethanolamine oleate added to an organic solvent such as high-flash naphtha or kerosene; or aqueous alkaline solutions, applied either by immersion or electrolytically. These methods may be used individually or in conjunction with one another.

The bluing methods may be divided into three general classes:- temper-coloring or heat-tinting, coloring in chemical solutions, and coloring by electrolytic methods. Most of these films or coatings provide only slight protective value against corrosion, unless oil, wax or lacquer is applied to the surface subsequent to the coloring.

III. TEMPER-COLORING OR HEAT-TINTING IN AIR

1. Interference colors.

A good blue may be obtained on iron and steel by heat-tinting (temper-coloring) the work in air or other oxidizing atmospheres. The color is produced by the interference of light in a thin surface film of iron oxide. As the thickness of the oxide film increases, the following sequence of colors is obtained:- light straw, straw, dark straw or a light golden brown, brown or bronze, purple, dark blue, and light blue. Further heating (with oxidation) produces the "second order" of interference colors in the same sequence, but they are usually less intense and consequently less pleasing. Further oxidation beyond the second order gives very indistinct colors.

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* Figures in brackets indicate the literature references listed in section VII.

In general, the thoroughly cleaned article is placed in an oven or furnace or on a hot metal plate, and the heating is continued until the desired color is obtained. It is then removed, cooled in water and dried. The dry surface may then be coated with a suitable light transparent lacquer or with a film of oil by immersion in a heated light oil (such as boiled linseed oil). Greater protection against corrosion is secured in this manner.

The period of heating required to obtain any specific color desired depends chiefly upon three factors:- the temperature of the oven or furnace, the composition of the steel, and the size and shape of the article.

2. Time-temperature relationship.

The dependence of the period of heating upon the temperature of the article during the bluing treatment has been studied in detail in an investigation carried out at the National Bureau of Standards. Readers who are interested in the theoretical aspects of the subject should consult the published report [10]. The rate at which a desired color can be obtained on steel varies somewhat with the composition of the steel. This is not an important factor, however, unless the differences in composition are very pronounced, for example, open-hearth iron vs. stainless steel. The rates for the heat-tinting of the carbon steels and the low alloy steel used in this present investigation were not influenced greatly by the composition of the steel. The blue may readily be obtained on these steels by heating in the temperature range of 500 to 700°F. (260 to 370°C), the period of heating varying from about 3 or 4 hours to one minute respectively for the extremes of this temperature range. The cast iron that was used blues at a slightly lower rate than the open-hearth iron or the steels and, consequently, it requires a little longer period of heating, or a slightly higher temperature.

The temper-coloring of steels, as well as the bluing in molten salt baths described in section IV, influences the physical properties, because tempering of the steel takes place at these temperatures. Hardened steels are softened somewhat by these processes. Consequently bluing in aqueous solutions at lower temperatures, or electrolytic coloring, may be preferable when it is desirable to maintain the full hardness of the steel.

3. Influence of the size and shape of the article.

The size and shape of the articles are important practical factors that influence the heat-coloring. A large object requires a longer period of heating than does a smaller one, because of its greater heat capacity, and the consequently longer period of heating required to bring the temperature of the object up to that of the oven or furnace. In irregularly shaped articles, the thinner sections reach the temperature of the furnace more rapidly than do the thicker sections and thus color faster. This may result in non-uniform bluing of the article. This effect can be minimized by placing the article in the cool furnace and allowing it to heat up with the furnace.

The selection of the best operating temperature of the furnace should be determined by a few preliminary tests. If the heating period is so short that the bluing occurs in only a minute or less, the color may not be very uniform. In this case heating at a lower temperature with a correspondingly longer heating period generally gives a more uniform blue, especially with irregularly shaped objects.

4. Coloring by preheating.

Steel strip or wires may be blued by passing them through a bath of molten lead or a low-melting alloy. The color develops only after the steel leaves the bath and comes in contact with the air. The amount of the oxidation, and hence the color, are controlled by adjusting the temperature of the bath and by passing the steel strip or wire through a quenching medium, such as a water bath, when it has developed the desired color.

IV. COLORING IN MOLTEN SALT BATHS.

1. Time-temperature relationship.

Very good blue can be obtained on iron and steel by immersion in molten salt baths. The surface of the steel is oxidized by the oxygen liberated in the salt bath, and temper colors, the same as those formed by heating in air, are obtained. The molten salt also serves as an excellent means of heating the article uniformly, and hence is an aid in coloring it evenly. The time-temperature relationships for the formation of these colors are very similar to those obtained by heating in air [10]. The materials used in this investigation colored slightly more slowly in the molten nitrate and nitrite baths than they did in air at the same temperature.

2. Composition of baths and operating conditions.

For bluing with the molten salts, either sodium or potassium nitrate or nitrite may be used. A mixture of the sodium and potassium salts is preferable to either alone, because of the lower melting point of the mixture. This permits the coloring to be carried on at lower temperatures, and thereby furnishes better control, because the period of heating is increased and the oxidation can be stopped more easily at the desired color. Some of the salt usually solidifies on the surface of the object immediately upon its immersion in the bath, but melts again in a short time as the temperature of the article rises. This causes non-uniform bluing if the solidified salt is not melted from all of the surface at about the same time, because coloring occurs only when the surface of the article is in contact with the molten salt. In a bath having a low melting point, the amount of salt that solidifies on the object is much less, and it melts more readily, facilitating uniform coloring.

Several salts and salt mixtures were used in the tests on which this discussion is based. The salt baths of the compositions listed below were found to be the most satisfactory.

	Parts by weight
A. Potassium nitrate, KNO_3	100
Sodium nitrate, $NaNO_3$	100
Used at a temperature of about 625°F	(330°C)

	Parts by weight
B. Potassium nitrate, KNO_3	100
Sodium nitrate, $NaNO_3$	100
Manganese dioxide, MnO_2	5 to 10
Used at a temperature of about 625°F	(330°C)

	Parts by weight
C. Potassium nitrite, KNO_2	110
Sodium nitrite, $NaNO_2$	90
Used at a temperature of about 660°F	(350°C)

The salt bath may be melted in a cast iron or steel pot that is free from rust and has a shape and size to suit the articles to be blued. For small articles a short section of a steel pipe closed at one end with a pipe cap is suitable.

The same procedure is followed with all of the different salt baths. The articles should be thoroughly clean, free from rust and free from moisture. Moisture on them at the time of immersion may cause severe spattering of the molten salt. The articles are so suspended as to be completely covered by the molten salt until the desired color has been attained. (The article may be temporarily raised out of the bath to facilitate observation of the coloring.) After the desired blue has been obtained, the article is withdrawn and quenched in clean cold water to stop the oxidation, then immersed in boiling water to remove any salt remaining on the work, and finally dried. To obtain greater protection against corrosion or wear, the blued articles may be dipped in hot oil or finished with a light transparent lacquer or varnish. Finishing with a lacquer that has been lightly tinted blue usually improves the appearance.

Salt bath B is the same as A except for the manganese dioxide. This should be added after the temperature of the molten salt bath has been raised to about 900°F (495°C), after which the bath is allowed to cool to about 625°F (330°C) before using. All suspended matter should be allowed to settle to the bottom of the pot before the articles are immersed, otherwise discolored spots will appear on the blued surface.

The addition of manganese dioxide is optional. Although its omission has been reported [8] to give inferior results, in the tests in this investigation good results were obtained both with and without the addition of the manganese dioxide to the bath. Manganese dioxide gives a light green color to the nitrate bath and a darker green to the nitrite bath, which is somewhat disadvantageous as it makes the observation of the bluing difficult to follow while the work is suspended in the bath. Additions to the fused bath of other oxidizing agents, such as potassium permanganate, sodium perborate, or sodium peroxide proved disadvantageous. These additions, making the bath less transparent, hindered the observation of the progress of the coloring and produced less uniform blue.

Tests were made with the fused nitrate and nitrite baths to determine if, as has been reported, the addition of sodium hydroxide would improve the coloring. No improvement was noted with small additions and a decidedly deleterious effect was noted with additions of 10 percent or more, the color being non-uniform and very spotted. Unsatisfactory results were also obtained with fused sodium hydroxide baths, with or without the addition of nitrates and other oxidizing agents, such as manganese dioxide and potassium permanganate. A non-uniform blue with a very poor appearance was then obtained.

V. COLORING IN AQUEOUS SOLUTIONS

1. Advantages and limitations

Numerous formulas for the bluing of iron and steel in aqueous solutions are given in the technical literature. Only a few of the more highly recommended formulas could be tested and only those which gave the most satisfactory results are listed here. These results must not be considered as comprising a complete survey of this field. In general, the blue obtained with aqueous solutions differs considerably in appearance from that obtained by heat-tinting, although in both cases it is mainly due to interference colors. The specific color of the surface film itself has a great influence on the "over-all" appearance, this being especially noticeable in the case of the "luster washes", in which the precipitated surface film of lead sulphide has a characteristic "soft" appearance. Moreover, the blue obtained with aqueous solutions is always less brilliant and less intense than that formed by heat-tinting. A good light blue can be easily obtained but it is difficult to obtain one corresponding to the dark blue or violet temper color. The aqueous solutions are used at a much lower temperature than that of the molten salt baths and consequently the correct operating conditions can be maintained much more easily. Hardened steels can be blued by this method with very little, if any softening.

2. Cleaning procedure.

As in the previous methods, the articles must be thoroughly clean. A method found to be very satisfactory for preparing articles to be colored in an aqueous solution was as follows:- The rust-free article was first cleaned with an organic solvent (acetone, carbon tetrachloride or trichloroethylene). This was followed by electrolytic cathode cleaning in an alkaline solution, such as is generally used in electroplating. Electrolytic cleaning is faster and preferable to immersion alkaline cleaning. The following solution, at a temperature of about 195°F (90°C), proved suitable:

	g/l	oz/gal
Trisodium phosphate, $Na_3PO_4.12\ H_2O$	30	4
Sodium hydroxide, NaOH	10	1.5

A steel anode was used and a voltage of 4 to 5 volts was applied with the article serving as the cathode. The articles were then rinsed in water, dipped in a weak sulphuric acid solution (approximately 5 percent solution) for a few seconds, rinsed thoroughly in clean water and immediately immersed in the coloring solution.

3. Formulas and operating conditions.

Unless otherwise noted, all the following formulas refer to aqueous solutions, in which the required weights of the materials are dissolved in water and sufficient water is added to make a final volume of 1 liter or 1 gallon.

A very pleasing blue may be obtained on iron and steel by using "luster washes". An adherent lead sulphide film is precipitated on the surface of the immersed article and this produces interference colors which are modified somewhat by the specific color of the lead sulphide. Hence the appearance is different from the interference colors of the oxide films formed by heat-tinting.

Good "luster colors" were obtained with the following four solutions, the blue produced by solution D being slighter better than that of the other solutions.

		g/l	oz/gal
D.	Sodium thiosulphate (hypo), $Na_2S_2O_3 \cdot 5H_2O$	200	27
	Lead acetate, (sugar of lead) $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$	20	2.5
	Potassium acid tartrate, $KHC_4H_4O_6$	25	3.0
	Used at approximately 105°F (40°C).		

		g/l	oz/gal
E.	Sodium thiosulphate (hypo), $Na_2S_2O_3 \cdot 5\ H_2O$	70	10
	Lead acetage, (sugar of lead) $Pb(C_2H_3O_2)_2 \cdot 3\ H_2O$	20	3
	Used at 160 to 175°F (70 to 80°C).		

		g/l	oz/gal
F.	Sodium thiosulphate (hypo), $Na_2S_2O_3 \cdot 5H_2O$	10	1.5
	Lead acetate, (sugar of lead) $Pb(C_2H_3O_2)_2 \cdot 3H_2O$	10	1.5
	Used at approximately 195°C (90°C).		

	g/l	oz/gal
G. Sodium thiosulphate (hypo), $Na_2S_2O_3.5H_2O$	30	4
Lead nitrate, $Pb(NO_3)_2$	8	1
Ferric nitrate, $Fe(NO_3)_3.9H_2O$	3	0.4

Used at 160 to 175°F (70 to 80°C).

The salts should be dissolved separately in portions of the water and then mixed just before using. The cleaned article is immersed in the heated solution and moved to and fro until the desired color appears, whereupon it is rinsed, first in cold water, next in boiling water, and then dried and wiped over with a clean soft cloth. The colored surface may be coated with wax, or a transparent lacquer or varnish as a final treatment.

It is advantageous to use the solution at the lowest operating temperature since the bath is then most stable and the lead sulphide film formed at a low temperature adheres more tightly.to the basic metal [7]. Although solution D may be used without the addition of the potassium acid tartrate, the coloring rate is decreased and either a longer immersion period or a higher bath temperature is required. Solution F, which has the lowest concentration of sodium thiosulphate, required the highest temperature. The concentration of these solutions or of their constituents may be varied considerably and still furnish good coloring, although this may require a change in the temperature of operation.

A light blue on iron and steel may be obtained with either of the two solutions given below:

H. Arsenious oxide, As_2O_3	85 g/l	11 oz/gal
Hydrochloric acid, HCl (sp. gr. 1.18)	630 ml/l	80 fl. oz/gal

Use at approximately 195°F (90°C)

	g/l	oz/gal
I. Sodium nitrate, $NaNO_3$ or potassium nitrate, KNO_3	400	55
Sodium hydroxide, NaOH	400	55

Use at approximately 255°F (125°C).

The article, cleaned as given above, is immersed in the heated solution until the desired color is attained, whereupon it is rinsed thoroughly in cold water, then in boiling water and dried. If desired, it is given a final finishing treatment as described previously.

A blue-black or gray-black on iron or steel can be obtained by treatment with the following solution:

		g/l	oz/gal
J.	Ferric chloride, $FeCl_3.6H_2O$	90	12
	Mercuric nitrate, $Hg(NO_3)_2$	90	12
	Hydrochloric acid, HCl (sp. gr. 1.18)	90 (77 ml)	12 (10 fl oz)
	Alcohol, C_2H_5OH	360 (460 ml)	48 (40 fl oz)
	Water, H_2O (balance)		

The article (preferably cleaned with an alkaline cleaner) is immersed for 20 minutes, removed and allowed to dry for about 12 hours, after which the immersion and drying operations are repeated. The article is then placed in boiling water for 1 hour and dried again. The colored surface is finished by lightly scratch-brushing and oiling or waxing.

A gun-metal blue or gray can be obtained on iron or steel by immersion in the following solution:-

		g/l	oz/gal
K.	Ferric chloride, $FeCl_3.6H_2O$	200	25
	Antimony chloride, $SbCl_3$	4	0.5
	Gallic acid, $C_6H_2(OH)_3COOH.H_2O$	4	0.5

This solution is used hot, at a temperature of 160°F (70°C) or higher. The cleaned article is immersed in the bath until the desired color is attained, whereupon it is rinsed thoroughly in cold water, then in hot water, and dried. The finishing treatment is similar to those previously described.

VI. COLORING BY ELECTROLYTIC METHODS

1. Types and controlling factors.

Some of the electrolytic methods consist in the electroplating of copper or other metals on the article, with subsequent coloring of the plated metal layer by an appropriate method. However, as the present study was limited to the direct bluing of iron and steel, these indirect methods were not included. Cathodic coloring, anodic coloring, and coloring with the article serving alternately as anode and cathode were examined. More precise control is required with electrolytic methods than with heat-tinting or bluing in aqueous solutions. The coloring is influenced greatly by the initial surface condition (cleanliness and type of finish) and also by the chemical composition of the steel. A slight difference in the chemical composition may cause an appreciable variation in the coloring rate and necessitate a change in the voltage and the current density.

The blue obtained on iron and steel with these electrolytic methods is not so brilliant and intense as that obtained by heat-tinting in air or in salt baths. It is obtained, however, at lower temperatures, which is often very advantageous, especially in the case of fully hardened steels.

2. Cathodic coloring.

A light blue can be obtained by cathodic treatment in the following solution:-

		g/l	oz/gal
L.	Sodium hydroxide, $NaOH$	35	5
	Arsenious oxide, As_2O_3	35	5
	Sodium cyanide, $NaCN$	7	1

The solution is prepared by dissolving the arsenious oxide and sodium hydroxide in hot water and then adding the sodium cyanide to the cool solution. A plating tank or other suitable vessel equipped with carbon anodes is used. The carefully cleaned article (electrolytic alkaline cleaning preferred) is made the cathode and a potential of about 2 volts is applied. A current density of 2 to 7 amperes per square foot is required. The current density should be adjusted to suit the size and the composition of the steel and is best determined experimentally. A treatment of 1 to 3 minutes is usually sufficient to blue the article, whereupon it is removed, washed in hot water, dried, and if desired, finished as previously described.

3. Anodic coloring.

The following solution has been recommended for producing a light blue on iron or steel by anodic treatment. However, the results obtained in the experimental tests were not very satisfactory because of non-uniformity of the color.

		g/l	oz/gal
M.	Lead nitrate, $Pb(NO_3)_2$	8 - 80	1 - 10
	Ammonium nitrate, NH_4NO_3	10 - 50	1.5 - 7

(Haswell, U. S. Patent 453,355, June 2, 1891).

This solution is used at a temperature ranging from 65 to 75°F (18 to 24°C) and with a current density of 5 to 10 amperes per square foot (1/2 to 1 ampere per square decimeter), a potential of about 2 volts being required. The cleaned article, used as anode, is treated for a period of about 10 minutes until the desired color is obtained, whereupon it is removed, washed in hot water, dried and finished as previously described.

4. Alternate anodic and cathodic coloring.

A blue or blue-black can be obtained on iron or steel with an electrolytic method, the article to be blued being used alternately as anode and cathode (Jermain's U. S. Patent, 1,342,910 of June 8, 1920). The following solution is used:-

		g/l	oz/gal
N.	Sodium nitrate, $NaNO_3$	150	20
	Sodium hydroxide, $NaOH$	375	50

The temperature of the bath is held at 250 to 255°F (120 to 124°C), that is, just below the boiling point of the solution. The cleaned article is used as anode against a carbon cathode for five minutes with a current density of approximately 50 amperes per square foot (4.5 amperes per square decimeter), after which the current is reversed for the same period, the article serving as cathode and the carbon as anode. This cycle is preferably repeated three times. After removal from the bath, the article is washed, dried, and finished in accordance with previous directions. A lighter blue with less gray or gray-black may be obtained by decreasing the coloring periods to 2 or 3 minutes. Stirring of the bath is advisable, as it promotes uniformity of coloring.

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